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作品名稱 **Synthesize Sodium Sesquicarbonate and Increase Yield**

得獎獎項

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關鍵詞 **Sodium Sesquicarbonate、yield、diaper ash**

作者照片

Abstract

In order to recycle disposable diapers, we investigated the conditions where sodium sesquicarbonate (Chemical formula $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ hereinafter called sesqui) precipitates selectively from sodium carbonate and the conditions for high yield. For the selective precipitation of sesqui, we defined the time required for the reaction solution to pass through the sesqui precipitation area in the Na_2CO_3-$NaHCO_3$-H_2O phase diagram (45°C) as Δt. As a result, we revealed that Δt is involved in the selective precipitation of sesqui, and that we can synthesize sesqui without the expensive addition of L-Arginine as used in a previous research. Also, we proposed the "Stay method", in which the supply of CO_2 is stopped for 30 minutes to the lengthen the Δt, and found that we could synthesize sesqui selectively even under conditions in which sodium bicarbonate is likely to be precipitated as well.

Regarding the high yield of sesqui, the yield was greatly improved by the common ion effect of Na by adding NaOH to the reaction solution, sesqui synthesis by repeated reactions with CO_2, and sesqui recovery by adding the anti-solvent ethanol, reaching a sesqui conversion rate of 95%. This means 109 g of sesqui can be synthesized from 100 g of Na_2CO_3. Moreover, we confirmed that these synthesized samples have almost the same detergency as commercial sesqui.

We did a test calculation to reveal the usefulness of this research. First, if diaper recycling technology is put into practical use and all used diaper waste in Saijo City can be recycled, a reduction of 534 t/year of used diaper waste can be expected. This corresponds to a 2.3% reduction in Saijo City's waste output. From the ash that would ultimately remain after being recycled, we expect up to 35.3 t/year of synthesized sesqui using our experimental method. In addition, a CO_2 reduction of 8.2 t/year is possible in the process, which is about equivalent to the volume of one gymnasium.

1. Introduction

Reducing the amount of garbage in Saijo City is one of main tasks in achieving SDGs (Sustainable Development Goals). Our school is located in Saijo City, Ehime. The household waste output of Saijo City is 23,682 t/year at present.[1] Saijo City's waste output has consistently been recorded as the largest of any other city in Ehime Prefecture.[2] The amount of disposable diaper garbage is estimated to be 1,101 t/year.[1] Kao Corporation, which has a diaper manufacturing plant in Saijo City, is working on carbon recycling of disposable diapers garbage which needs large amounts of energy to be disposed.[3] Although diaper ash is produced in this process, no effective way to use this had been established. Therefore, we can contribute to achieving our city's SDGs by utilizing diaper ash.

The main component of diaper ash is Na_2CO_3. There are industrial ways to resynthesize sodium sesquicarbonate (Chemical formula $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ hereinafter called sesqui) from Na_2CO_3.[4)5)] Sesqui, which is used to make alkaline detergents, is less harmful to our skin and is better at effective removing proteomic stains like blood than sodium bicarbonate because of its stronger alkaline. Today, sesqui is made from the natural resource trona.[6)] However, only two studies have been conducted on synthetic sesqui, which strongly relies on natural resources.[4)5)] Additionally, conditions for efficiently manufacturing high yields of sesqui have not been established nor sufficiently investigated.[5)] Sesqui is a limited natural resource, so synthesized sesqui has significant importance from the perspective of sustainable development.

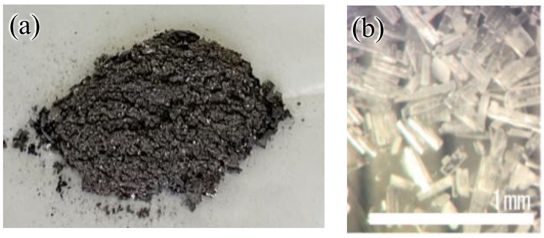

Fig.1 (a)Diaper Ash (b)Sesqui Crystals

2. Purpose of the Study

By reacting a solution of Na_2CO_3 with CO_2, sesqui can be selectively precipitated. However, the efficacy of the additive L-Arginine was unclear, and a highly efficient way of manufacturing sesqui has not yet been investigated enough.

Therefore, the purpose of this research was to identify the conditions for the selective precipitation of sesqui and the conditions for producing a high yield.

3. Research Methods

3.1. Outline

Below, we show the outline of our experiment. (Fig.2) Firstly, sesqui was synthesized by repeatedly reacting CO_2 with Na_2CO_3. (Experiment 1) Secondly, we added ethanol as anti-solvent to the filtration to increase the yield. (Experiment 2) Thirdly, we conducted simple detergency tests to evaluate the synthetic samples. (Experiment 3)

In this study, we investigated the selective precipitation conditions of sesqui and those for achieving a high yield by analyzing the synthetic samples obtained in Experiments 1 and 2. Furthermore, a simple detergency test was conducted in Experiment 3 on those synthetic samples we expected to produce high yields.

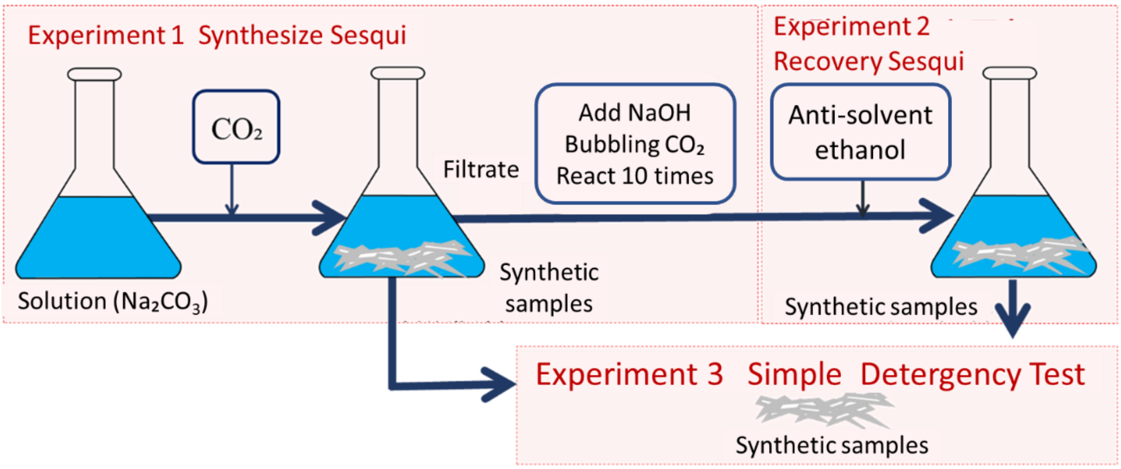

Fig.2 Outline

3.2. Experiment 1: Synthesize Sesqui (1st Reaction with CO_2)

Following the previous research, we added CO_2 to solutions of Na_2CO_3, that was prepared according to compositions shown in Table 1. CO_2 bubbles were generated at 100 mL/min with a silicon tube at the bottom of a triangular flask containing the reaction solution and supplied until crystals began to precipitate (Fig.3). In a specific condition, the CO_2 supply was stopped for 30 minutes and then resupplied.

During the reaction, we measured the change in pH over time. We stirred solutions for 24 hours after the crystals precipitated, then filtered the synthetic sample for 48 hours at 45℃ and dried. Also, in specific conditions, we added NaOH to the resulting filtrate and repeated the reaction 10 times with CO_2. After, we measured the mass of the synthetic samples, observed the crystals' morphology using a stereomicroscope (Ricoh SMZ-1000N), and identified the crystal phase using an X-ray diffractometer - XRD (Rigaku MultiFlex Corporation).

In condition 8, we stopped the supply of CO_2 for 30 minutes, while the solution was in the sesqui precipitation area, and then resupplied it. We named this the "Stay method". Thus was based on phase diagram.

We reacted for 10 times in condition 6-8 and checked crystal phase.

Table1 The component of solutions (First reaction with CO_2)

		1	2	3 [5)]	4	5	6	7	8
Na_2CO_3		100	100	100	100	100	100	100	100
H_2O		250	250	250	250	250	250	250	250
NaOH		6	6	6	6	6	6	—	6
NH_2 Group Compound*1	L-Arginine	—	—	25	12.5	6.3	—	—	—
	Urea	—	8.7	—	—	—	—	—	—
	Glycine	21.6	—	—	—	—	—	—	—

*1 Each has same number of NH_2 group which catches CO_2.

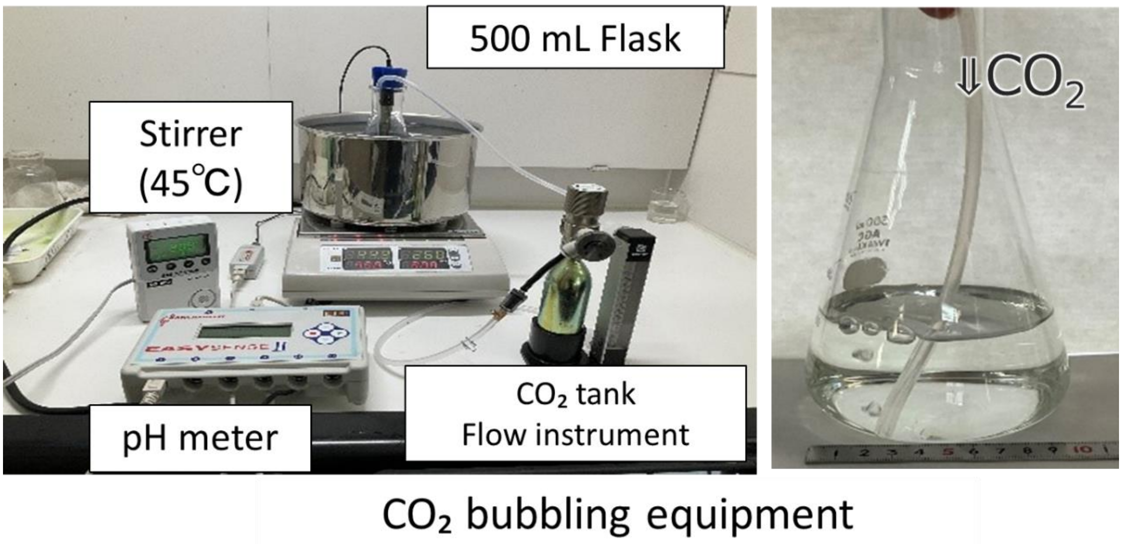

Fig.3　Sesqui Synthesis

3.3. Experiment 2: Recovery sesqui (Adding anti-solvent)

175 mL of anti-solvent ethanol was added using a commercially available drip device, at 1mL per minute, to the filtrate obtained by repeated reactions with the CO_2. The resulting synthetic sample was filtered and then dried for analysis.

3.4. Experiment 3: Simple Detergency Test

We made a contaminated cloth by putting 5.0 μL of pig's blood on cotton fabric and air-drying it for 10 months. 2.0% aqueous solutions[7] of the synthetic sample obtained under each condition and commercial sesqui were prepared and the contaminated cloth were soaked in 5.0 mL of the aqueous solutions for 24 hours to evaluate the degrees of stain removal. We also conducted this test using pure water.

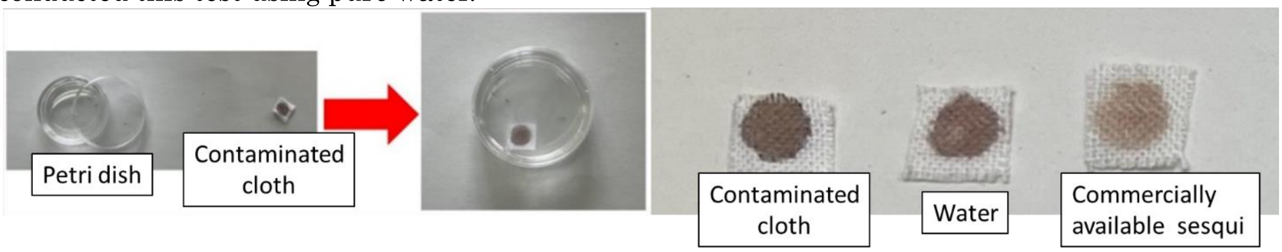

Fig.4　Simple Detergency Test

4. Result and Discussion - Investigation of the Conditions for Selective Precipitation of Sesqui

4.1. Sesqui Synthesis (1st reaction with CO_2)

We all synthetic samples have some hundreds of μm needle-like crystal and some samples have crystal of sodium bicarbonate.

First, we found that needle-like crystals of sesqui of several hundred μm were formed under all conditions, and that sodium bicarbonate and other substances were also formed under some conditions. The crystal forms and yields (Table 2), micrographs (Fig.5) are shown. We compared the expected peaks of each compound and identified the crystal phases by overlaying them with the XRD profiles of the synthetic samples. [8)9)10)]

We now focus on the Na_2CO_3-$NaHCO_3$-H_2O phase diagram (45°C), the presence of carbonic ion, and pH. First, the reaction between the solution and CO_2 gradually decreases the pH and increases HCO_3^- as shown in Fig.6.[11)] In addition, a sesqui precipitation area exists in the Na_2CO_3-$NaHCO_3$-H_2O phase diagram (45°C), as shown in Fig.7 [12)]; as the reaction with CO_2 proceeds, HCO_3^- increases and the reaction shown by the red arrow in Fig.7 proceeds and begins to pass through the sesqui precipitation area. Therefore, using the fact that the pH of the reaction solution measured during the experiment corresponds to the relative ion abundance ratio, the time for the reaction solution to pass through the sesqui-precipitation area was defined as Δt〔min〕, as shown in Fig.8. Due to this relationship, Δt was used an indicator to determine the selective precipitation of sesqui.

Only in conditions 3, 6, 7 and 8, where the Δt was prolonged, did a lot of sesqui crystal structures form. Crystal precipitation could be visually confirmed at approximately pH 10.3 for conditions 1 to 7, and at approximately pH 10.5 for condition 8, all of which even began to form in the area of sodium bicarbonate precipitation. From these results, we found that the conditions with longer Δt remained longer in the sesqui precipitation area and produced a larger amount of crystal structures.

Looking at conditions 1 through 5 containing -NH_2 group compounds, sesqui was selectively obtained only in condition 3, which contained a large amount of the expensive additive L-Arginine. This is because solution stayed the sesqui precipitation area for a prolonged time due to the L-Arginine's pH buffering effect. Although Glycine has a pH buffering effect, it's ineffective inside the sesqui precipitation area. We found that the selective precipitation of sesqui is based on the length of the Δt and the pH buffering effect of L-Arginine. Moreover, we revealed the conditions for selective precipitation of sesqui without the use of expensive L-Arginine.

Table 2 Crystal phase in 1st CO_2 reaction

Condition		1	2	3 [5)]	4	5	6	7	8
Na_2CO_3		100	100	100	100	100	100	100	100
H_2O		250	250	250	250	250	250	250	250
NaOH		6	6	6	6	6	6	—	6
-NH_2 Group Compound	L-Arginine	—	—	25	12.5	6.3	—	—	—
	Urea	—	8.7	—	—	—	—	—	—
	Glycine	21.6	—	—	—	—	—	—	—
Crystal phase	Sesqui	○	○	○	○	○	○	○	○
	$NaHCO_3$	○	○	—	○	○	—	—	—
	$Na_2CO_3 \cdot H_2O$	—	○	—	—	—	—	—	—
Δt〔min〕		32	31	60	30	23	41	51	68

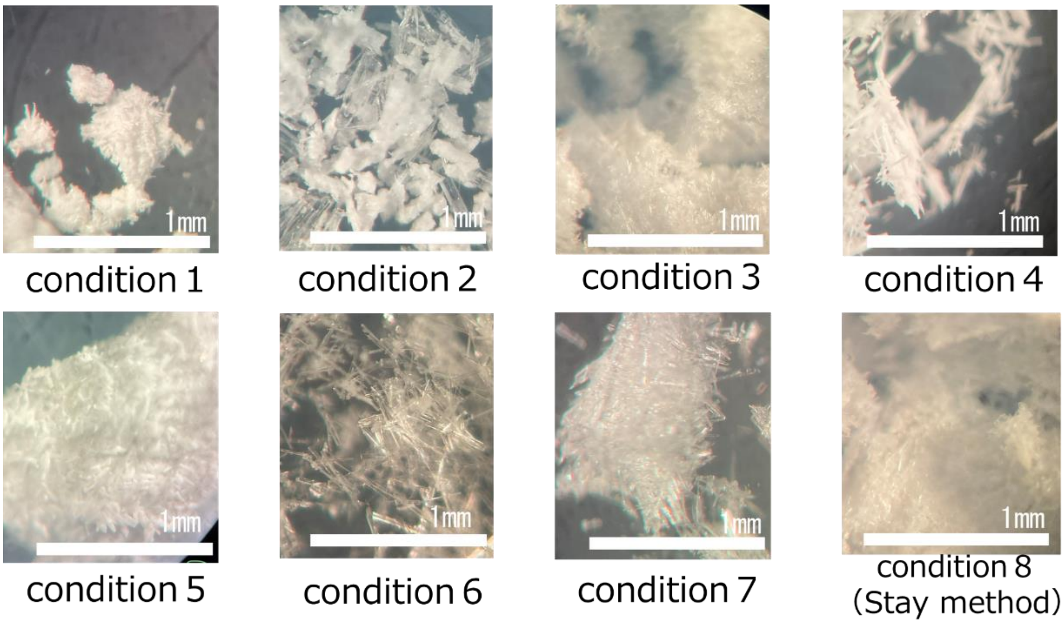

Fig.5 Microscopic Images of Synthetic Sample

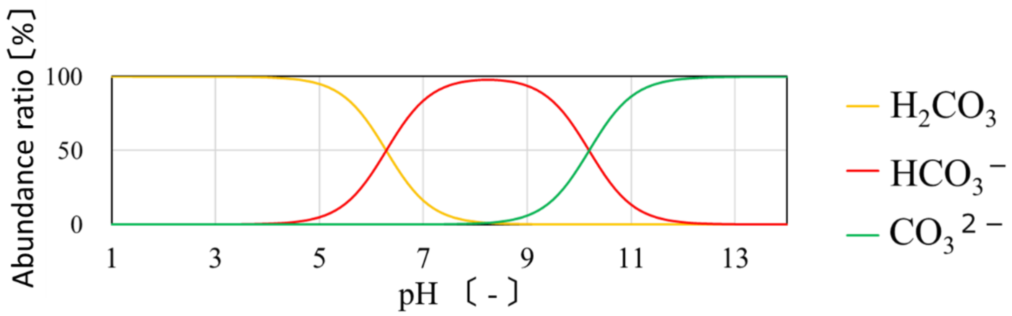

Fig.6　Abundance ratio of carbonic ion(45℃)[12)]

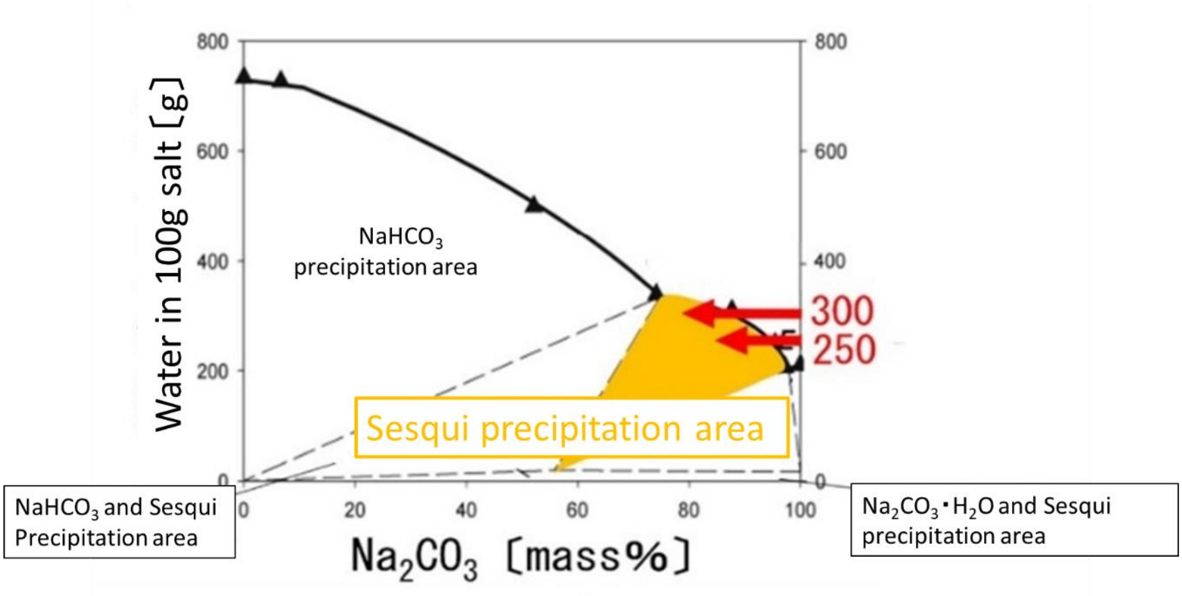

Fig.7　Na_2CO_3-$NaHCO_3$-H_2O phase diagram (45°C)[11)]

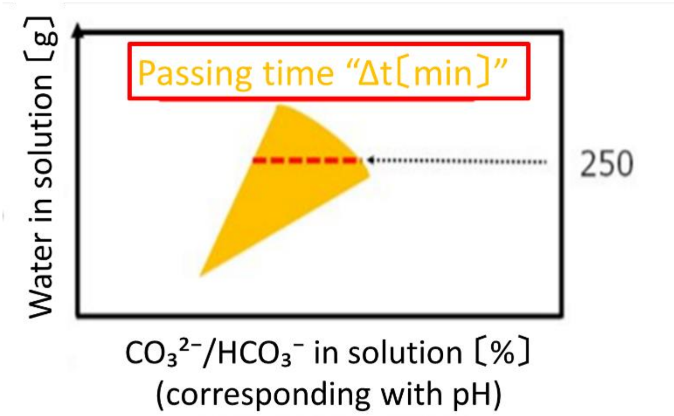

Fig.8 Definition of "Δt"

4.2. Sesqui Synthesis (Repeated Reactions with CO_2)

Of the conditions under which sesqui was selectively precipitated, conditions 6-8, in which L-Arginine was not added, are shown below, along with a list of crystal forms (Table 3) of the synthesized samples obtained by repeating the reaction with CO_2 10 times, and a micrograph of condition 8. (Figure 9) In conditions 6 and 7, $NaHCO_3$ was identified. On the other hand, in condition 8, where the CO_2 supply was temporarily stopped and Δt was prolonged, only sesqui was selectively obtained. This is an innovative method to selectively precipitate sesqui crystals without using expensive additives such as L-Arginine. We named this method the "Stay method". We enabled the selective precipitation of sesqui by utilizing our "Stay method", which focuses on prolonging the Δt and temporarily stopping the supply of CO_2.

Table 3 Crystal phase (Repeated Reactions with CO_2)

Condition 6		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Crystal Phase	Sesqui	○	○	○	○	○	○	○	○	○	○
	$NaHCO_3$	—	○	—	—	○	○	—	○	○	—
	$Na_2CO_3 \cdot H_2O$	—	—	—	—	—	—	—	—	—	—

Condition 7		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Crystal Phase	Sesqui	○	○	○	○	○	○	○	○	○	○
	$NaHCO_3$	—	○	—	—	○	○	○	○	—	—
	$Na_2CO_3 \cdot H_2O$	—	—	—	—	—	—	—	—	—	—

Condition 8 "Stay method"		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Crystal Phase	Sesqui	○	○	○	○	○	○	○	○	○	○
	$NaHCO_3$	—	—	—	—	—	—	—	—	—	—
	$Na_2CO_3 \cdot H_2O$	—	—	—	—	—	—	—	—	—	—

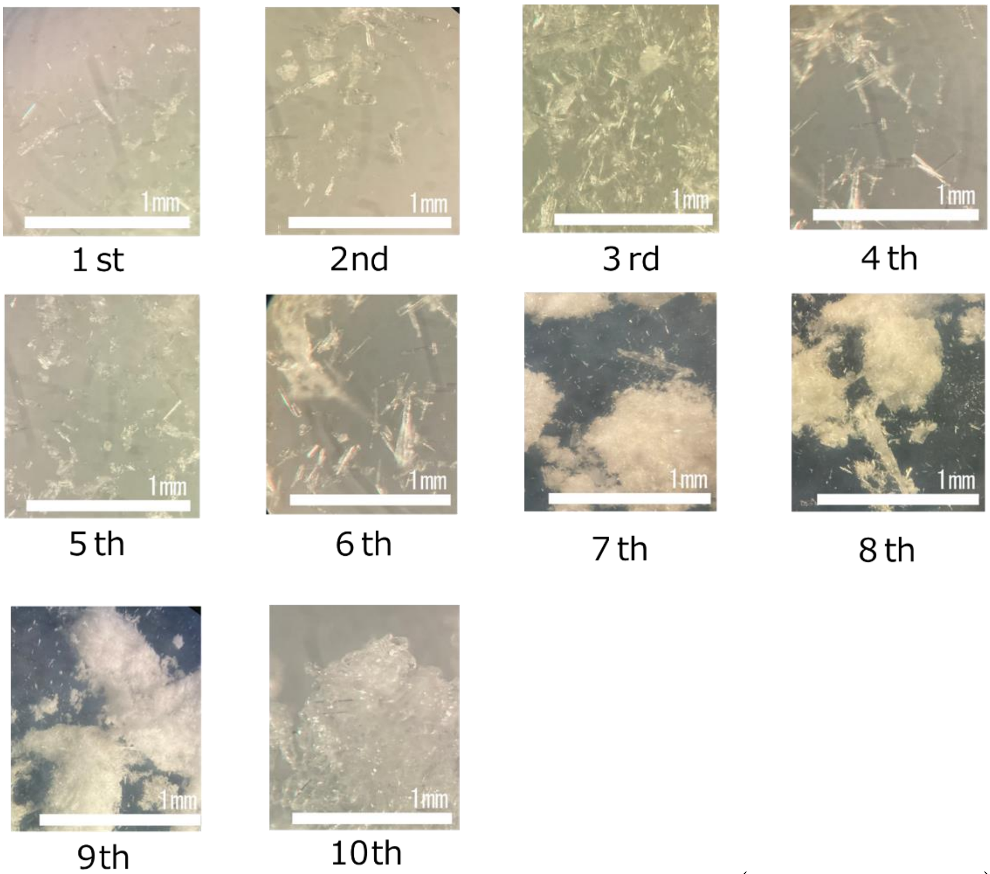

Fig.9 Repetition of Condition 8 ”Stay method” (Microphotograpgh)

4.3. Recovery sesqui

We added ethanol as an anti-solvent to the solution in condition 8, in order to get a higher yield of sesqui. Figure 10 shows the precipitation in condition 8. There are no needle-like crystals as before, but instead only sesqui was precipitated because of overlaying its crystal phase.. By adding ethanol gradually, the solubility was reduced and a greater amount of selectively precipitated sesqui was yielded.

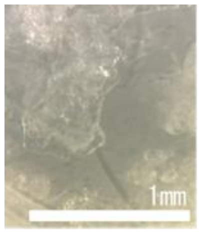

Fig.10 Adding Ethanol

5. Result and Discussion ― Conditions for a Higher Yield of Sesqui

5.1. Effects of adding NaOH (Sesqui Synthesis 1st reaction with CO_2)

Adding NaOH is an effective way to increase yield. Below we show the amount of yield in conditions 1 to 8. We focused on conditions 6 to 8, where only sesqui was precipitated without the addition of L-Arginine. The yield of condition 6 was 13.6 g heavier than condition 7. If Na_2CO_3 is produced by the reaction of NaOH and CO_2 , and all of it is converted to sesqui, we can estimate that 8.5 g of sesqui was precipitated. These results suggest that the amount of sesqui precipitated increased due to the common ion effect of Na in NaOH, and that the addition of NaOH is effective in improving the yield.

Comparing conditions 6 and 8, which both have the same component of the reaction solution, the yield of condition 6 was 9.6 g heavier. In the “Stay method” of condition 8, the pH at which precipitation began was pH 10.5, which was about 0.2 higher than the pH 10.3 of condition 6. This may be due to the large amount of crystallization, which accelerated the timing at which precipitation began to visually occur. However, the addition of NaOH seems to have resulted in an excess of Na^+ in the reaction solution. Therefore, we repeated the reaction with CO_2 10 times and compared the yields.

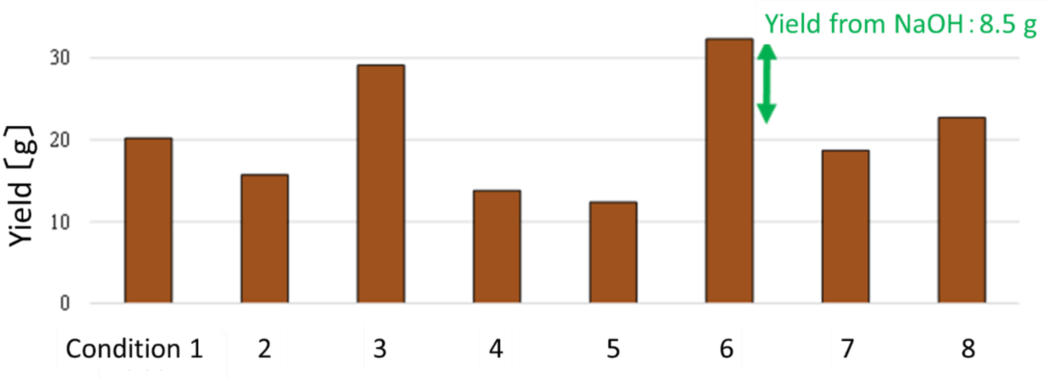

Fig.11　Yield of Synthetic Sample under each experimental condition

5.2.　Repeated Reactions with CO_2 and adding anti-solvent

In condition 6 and 8, where NaOH was added and in which we expected to precipitate a lot of sesqui, the reaction with CO_2 was repeated 10 times. We also added ethanol to the solution in condition 8, where only sesqui was precipitated. Then, we compared the total yields based on the following hypothesis and definitions.

・We assume that all NaOH reacted with CO_2, creating Na_2CO_3. We also assume that all Na_2CO_3 was converted to sesqui and that 8.5 g of sesqui was specifically created by the addition of NaOH.

・In the repeated reactions of conditions 6 and 8, a maximum of 200.1 g of sesqui was precipitated, 85 g of which was derived from NaOH.

・We assume that the composition of the synthetic sample was only sesqui, derived from both Na_2CO_3 and NaOH.

・We define a sesqui conversion rate as follow, and used to calculate the amount of sesqui that was derived from Na_2CO_3.

$$\text{Conversion rate〔\%〕} = \frac{\text{Yield of Synthesized Sample〔g〕}^{*1}}{\text{Theoretical Maximum Yield Except for Sesqui from NaOH}^{*2}\text{〔g〕}} \times 100$$

Fig.12 shows the conversion rate and total yield of each condition. In previous research, the solution was reacted only once so the yield and conversion rate were low. There was little difference in the total yield between conditions 6 and 8, which we subject to repeated reactions and it was much larger than previous research. In particular, condition 8, using the "Stay method", sesqui was selectively precipitated with a conversion rate of 61%. Moreover, by adding ethanol, the conversion rate reached 95%. This result means that we can get 109 g of sesqui ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) from 100 g of Na_2CO_3. It is clear that this method can convert almost all Na_2CO_3 to sesqui.

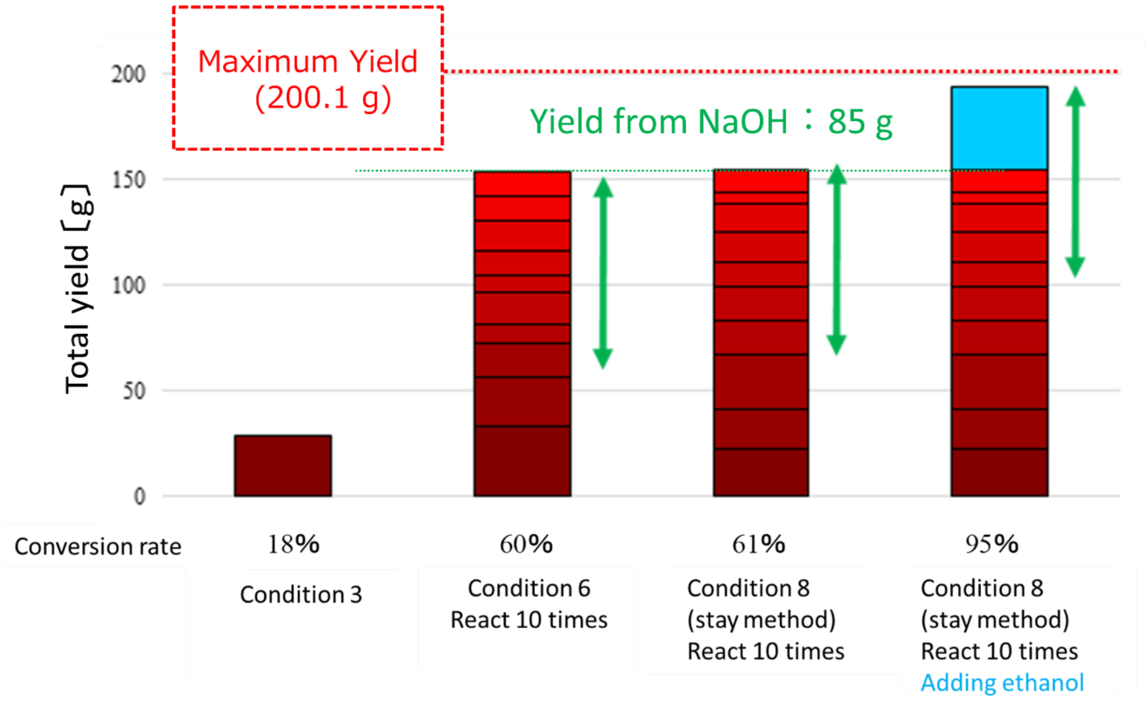

Fig.12 Total Yield comparing

5.3. Estimation of Research Results

According to the results and our assumptions, we estimate the usefulness of this study. The assumptions used are as follow.

・The amount of disposal garbage in Saijo City is 1,101 t a year. (estimation) [1)]

・For every 1 kg of disposable diaper waste in Saijo City, 50 g of diaper ash can be produced, of which 53% consists of Na_2CO_3 [13)]

・All disposable diaper waste in Saijo City could be converted to ash.

・95% of the Na_2CO_3 in diaper ash could be converted to sesqui in our experiment method. (According to the conversion rate of this study)

As a result, disposable diaper recycling technology could reduce Saijo City's waste by 534 t/year. This means a 2.3% reduction in the waste output of Saijo City. Using diaper ash made from recycling, 35.3 t/year of sesqui could be converted with our experimental method. Through this process, it will also be possible to reduce CO_2 emissions by 8.2 t/year. This is about as large in volume as one gymnasium.[14)]

6. Results and Discussion－Simple Detergency Test

Synthetic samples of sesqui, created using the "Stay method" have enough detergency to be competitive with commercial sesqui. Figure 13 shows the results of our detergency test. Pure water was able to remove some stains because of water-soluble proteins involved in blood, while commercial sesqui removed stains clearly. We found that our synthetic samples could remove stains just as well as the commercial sesqui. Although some of the blood stains remained in condition 6, all samples of condition 8 removed the stain equal to that of commercial sesqui. This may suggest that the additional mixing of sodium bicarbonate prevents a loss of detergency.

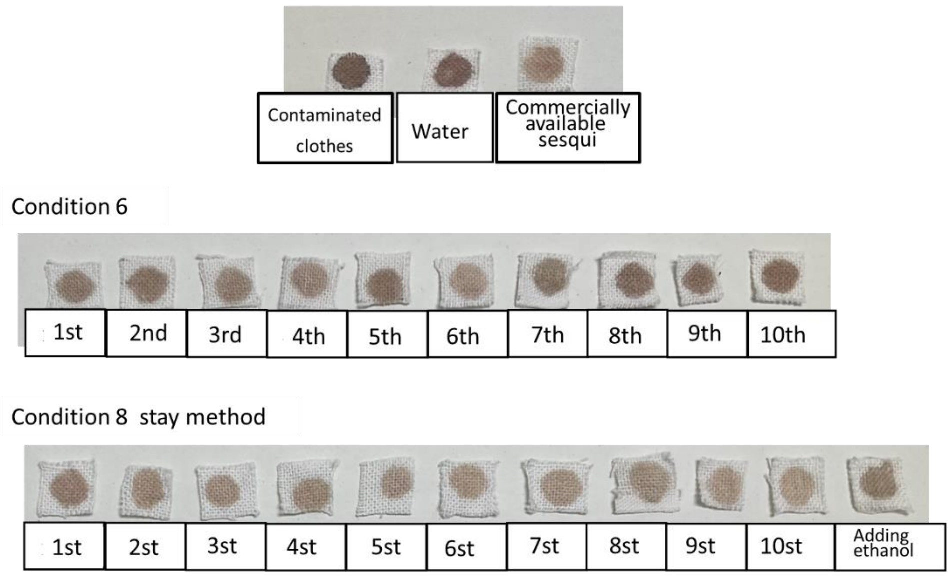

Fig.14 Simple Detergency Test

7. Conclusion

In this study, we investigate the conditions for selective precipitation of the reagent, Na_2CO_3-derived, sesqui, in large yields, in order to recycle disposable diapers. First, we defined the time required for the solution to pass through the sesqui precipitation area in the Na_2CO_3-$NaHCO_3$-H_2O system phase diagram (45℃) as Δt. As a result, we found that L-Arginine was effective in precipitating sesqui in previous research due to its pH buffering effect. Also, the longer the Δt, the more sesqui crystallization occurred, enabling us to selectively precipitate the sesqui. In addition, we proposed the "Stay method" in which we stop the CO_2 supply for 30 minutes so that the Δt is prolonged. This enabled us to selectively precipitate sesqui even if the solutionstay in $NaHCO_3$ precipitation area on phase diagram. From these results, we were able to precipitate sesqui selectively without using L-Arginine as used in previous research.

Next, we achieved a sesqui conversion rate of 95%. This is due to the following: the common ion effect of Na from the addition of NaOH to the reaction solution, repeated reactions with CO_2, and by adding ethanol as an anti-solvent. This means we could get 109 g of sesqui per 100g of Na_2CO_3. Moreover, these synthetic samples have almost the same detergency as commercially available sesqui.

The research estimates that disposable diaper technology could reduce waste by 534 t/year, which is equivalent to a 2.3% reduction in Saijo City's waste output. In this process, 8.2 t/year of CO_2 could be reduced, which is about the same volume as a gymnasium.

Our future task is to proceed with practical experiments using actual diaper ash and to deepen our understanding of the usefulness of this research, acquiring a more realistic view from an LCA (Life Cycle Assessment) evaluation.

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14) GHG Reduction Services Carbonoffset Bye-Bye CO_2

9. Acknowledgements

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【評語】030036

In modern era，waste recycling is critical for a sustainable society. This project utilized wastes from local industry and try to find a new approach for carbon fixation using diaper ashes. The initiative is novel and the research is reasonable and practical though not flashy.